

## Self-supported carbon electrodes obtained by tape casting

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This paper describes the preparation and electrochemical response of self-supported carbon electrodes prepared by tape casting. The dc electrical conductivity,  $\sigma$ , of the electrodes was determined by four-wire resistance measurements and a relation between the graphite/organic additives ratio and the electrical conductivity was established. The application of these self-supported carbon electrodes as working electrodes in analytical techniques was also evaluated using norepinephrine as electroactive substance in cyclic voltammetry and chronoamperometry. The results were compared with the traditional electrodes, carbon paste electrodes (CPEs), showing that the new self-supported carbon electrodes had both lower background noise and higher analytical response.

*Keywords: tape casting, self-supported carbon electrodes*

### Electrodos de carbono autosoportados obtenidos por colado en cinta.

Este artículo describe la preparación y respuesta electroquímica de electrodos de carbono autosoportados preparados mediante colado en cinta. La conductividad eléctrica en corriente continua de este nuevo tipo de electrodos de carbono se ha determinado usando el método de cuatro puntas y se ha establecido una relación entre la relación grafito/aditivos orgánicos y la conductividad eléctrica. La aplicación de estos electrodos autosoportados como electrodos de trabajo en diversas técnicas electroanalíticas también se ha evaluado, empleando norepinefrina como analito en voltametría cíclica y en cronoamperometría. Los resultados se compararon con los obtenidos empleando los electrodos de pasta de carbono tradicionales como electrodos de trabajo, viéndose que la señal de los nuevos electrodos autosoportados poseía menor ruido de fondo y mayor respuesta analítica.

*Palabras clave: colado en cinta, electrodos de carbono autosoportados*

## 1. INTRODUCTION

Since their introduction in 1958 by Adams, non-modified carbon pastes are normally used to prepare electrodes (Carbon Paste Electrodes, CPEs) as sensors in electroanalytical applications (1). CPEs usually consists of graphite powder and a non-conductive liquid binder such as nujol or uvasol (2,3). Along with CPEs, Chemically Modified Carbon Paste Electrodes (CM-CPEs) have been rapidly developed. In this case, the electrode consist of another constituent, known as modifier, that provide the sensor with the selectivity to a given reaction, for example, biological modifications of carbon pastes as enzymatic biosensors (4,5). The main features of these electrodes are homogeneity, high ohmic conductivity and stability.

The preparation of traditional CPEs involves the manual mixing of graphite powder and the liquid binder in an agate mortar. The homogeneous paste is then packed into a small cavity, 1-10 mm in diameter, at the end of a PVC or Teflon tube (1).

Tape casting has been widely used in electronics industry for the preparation of different devices (capacitors, piezoelectric actuators, etc) (6-8). No information about the substitution of ceramic powders by graphite in the tapes has been found in the literature. This processing method should

provide the possibility of the preparation of self-supported graphite tapes that can be used as electrochemical sensor in several techniques like voltammetry, amperometry, etc. Some advantages of the self-supported carbon electrodes are their strength and handling facilities.

The objective of this work is the preparation of a new kind of carbon electrodes using tape casting and their validation as electroanalytical sensors by determining the oxidation of norepinephrine in cyclic voltammetry and amperometry. Norepinephrine ( $C_8H_{11}NO_3$ ) is a catecholamine, also known as noradrenaline, which experiments redox reactions in carbon electrodes.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Preparation of Self-Supported Carbon Electrodes by Tape Casting

Six different self-supported carbon electrodes with different graphite/organic components ratio were prepared by tape casting. The raw materials were graphite powder (Fisher Scientific, Grade #38) with a density of 2.16 g/cm<sup>3</sup> and

the tape casting organic additives described elsewhere (9,10). The final graphite/organic additives ratio (after drying) were 90/10; 85/15; 80/20; 70/30; 60/40; 50/50 wt%. Particle size and agglomeration state of graphite powder were studied by means of a particle size analyzer (Malvern Instrument Ltd, Mastersizer S 2.18) and by Scanning Electron Microscopy (Carl Zeiss DSM 950).

The graphite powder was first mixed with the solvent and the dispersant in a ball mill for 2 hours, then the binders and plasticizers were added and mixed for an additional hour to obtain the slurry. The rheological behaviour of the slurry was characterized at room temperature using a viscometer (Haake, Rotovisco RV20). The tape casting was done in a discontinuous laboratory casting machine (ICV-CSIC) (11,12). The substrate was Mylar and the casting velocity  $6.5 \text{ cm}\cdot\text{s}^{-1}$  with an opening between the blades of 0.4 mm. Tapes were dried at room temperature and the thickness after drying was about  $100 \mu\text{m}$ . The microstructure of the top surface of green tapes was observed by SEM.

## 2.2 Preparation of Traditional Carbon Paste Electrodes (CPEs)

The traditional CPEs were prepared from same graphite powder and mineral oil (Sigma Aldrich) with a graphite/oil ratio of 90/10 wt%. These components were mixed in an agate mortar and packed in a teflon tube with an aperture at the end of the tube of 3 mm in diameter. The electrical contact was established through a stainless steel screw.

## 2.3 Electrical conductivity measurements

Green tapes were cut in rectangles of  $2.34 \times 1.0 \text{ cm}$  and Ag paste electrodes were applied, Figure 1.a. The dc electrical conductivity was determined by using the four-wire resistance

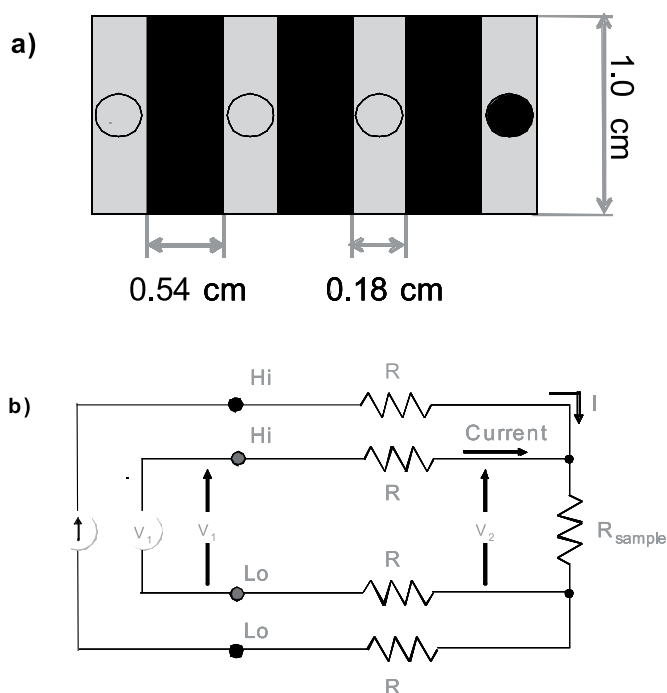


Fig. 1- a) Diagram of the self-supported electrodes for the four-wire resistance measurement. b) Equivalent circuit.

measurement method (13). This measurement method was chosen due to both the high electrical conductivity of graphite  $3 \times 10^6 \Omega^{-1}\cdot\text{m}^{-1}$  (along the six-fold axis) and  $5 \times 10^2 \Omega^{-1}\cdot\text{m}^{-1}$  (normal to the six-fold axis) and the flat configuration of the samples. The resistance due to the contact between the carbon tape and the Ag electrode is excluded from the measurements, Figure 1.b.

The dc electrical conductivity was determined by measuring the I-V curves with a multimeter (Keithley 2410). Since the material behaviour is ohmic, the resistance (R) can be obtained from the slope of the I-V curve. Knowing R ( $\Omega$ ), the distance between the electrodes, L (cm) and their area, A ( $\text{cm}^2$ ), the specific resistivity ( $\Omega\cdot\text{cm}$ ) can be calculated from

$$R = \rho L / A \quad [1]$$

and the specific conductivity  $\sigma$  (S/cm) is:

$$\sigma = 1/\rho \quad [2]$$

## 2.4 Electrochemical measurements

The electrochemical measurements were performed in an Electrochemical Analyser (BAS 100B) with a three-electrode electrochemical cell of 10.0 ml. The self-supported carbon electrode or the CPE was used as working electrode, the reference electrode was Ag/AgCl/KCl 3M (BAS Re-5B) and the auxiliary electrode was a Pt wire. The self-supported carbon electrode was prepared by cutting individual electrodes of 10 mm in length and 3 mm width. The final active surface,  $7 \text{ mm}^2$  was obtained by applying an acrylic non conductive paint. The potential to the working electrode was maintained constant (amperometry) or was linearly modified with time (cyclic voltammetry).

Cyclic voltammetry measurements were done using 50 mM phosphate buffer solution at pH 7.4 and norepinephrine  $1.0 \cdot 10^{-3} \text{ M}$ . The voltage scanning rate was  $300 \text{ mV}\cdot\text{s}^{-1}$ . Chronoamperometric studies were done in the same buffer solution. The working potential was adjusted at +0.500 V and the solution was stirred at 150 rpm. Seven successive additions of  $1.0 \cdot 10^{-5} \text{ M}$  of norepinephrine were done. Calibration curves were obtained from these amperometric measurements.

## 3. RESULTS AND DISCUSSION

### 3.1 Graphite Powder and Tape Casting Slurry Characterization

Figure 2 shows the SEM micrographs and the particle size distribution of graphite powder. As it can be seen, graphite powder was highly agglomerated with spherical aggregates of about  $15 \mu\text{m}$  (Figure 2.a) formed by smaller plate-like particles ranging from 1 to  $5 \mu\text{m}$  (Figure 2.b). The broad particle size distribution shown (Figure 2.c) agrees well with the high agglomeration of graphite powder ( $d_{50} = 16.48 \mu\text{m}$ ).

Tape casting slurries composed of different graphite/organic additives ratio were characterized by means of their rheological behaviour. In all cases, the slurries presented the pseudoplastic behaviour suitable for tape casting process. The viscosity at  $160 \text{ s}^{-1}$  increased with the graphite content from 1700 mPas for the 90/10 slurry to 900 mPas for the 50/50. In all cases, the viscosity was adequate for tape casting.

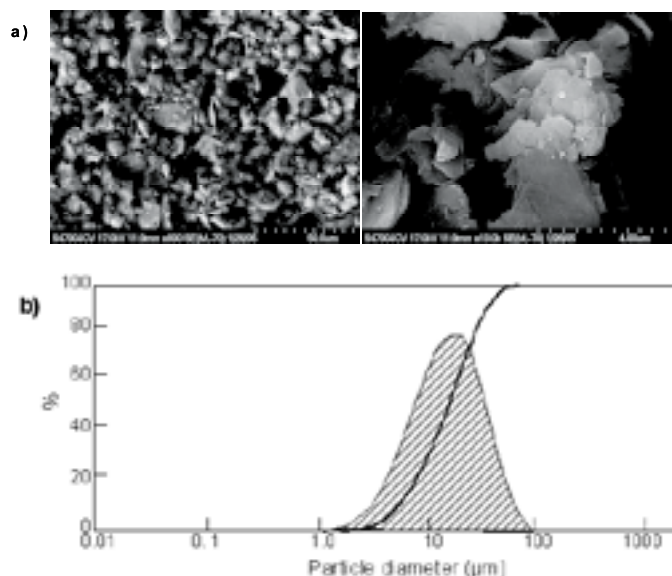


Fig. 2- a) and b) SEM micrographs and c) particle size distribution of graphite powder.

### 3.2 Electrical Conductivity

Figure 3 shows the I-V curves for the self-supported carbon electrodes as a function of the graphite/organic additives ratio. Table I resumes the dc electrical conductivity for each self-supported carbon electrode. As it can be seen, the electrical conductivity decreases with the decrease of graphite content in the tape, i.e., with the increase of organic additives. The change in electrical conductivity is almost two orders of magnitude when comparing 90/10 and 50/50 electrode. This behaviour is due to the formation of an isolating film onto the graphite particles which impedes the charge transference among the graphite particles. This isolating film grows with the increase of organic components. Figure 4 shows the SEM micrographs of the top surface of the 90/10 (Figure 4.a) and 50/50 (Figure 4.b) self-supported carbon electrodes. As it can be appreciated, in the case of 90/10 electrode graphite particles/agglomerates are easily distinguishable and they are very similar in size to the original graphite powder. On the contrary, in the 50/50 electrode graphite particles/agglomerates are very difficult to see because of the formation of the isolating film.

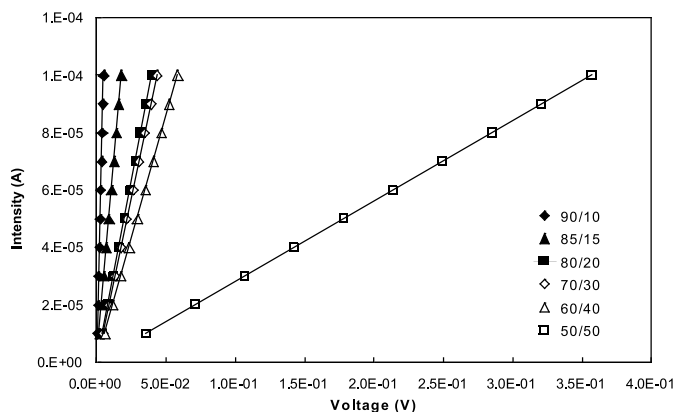


Fig. 3- I-V curves for the self-supported carbon electrodes as a function of the graphite/organic additives ratio.

TABLE I. ELECTRICAL CONDUCTIVITY (DC) OF THE SELF-SUPPORTED CARBON ELECTRODES.

Graphite/organic additives ratio	Conductivity, $\sigma$ (S/cm)
90/10	$6.3 \cdot 10^{-2}$
85/15	$1.7 \cdot 10^{-2}$
80/20	$7.5 \cdot 10^{-3}$
70/30	$6.9 \cdot 10^{-3}$
60/40	$5.1 \cdot 10^{-3}$
50/50	$9.0 \cdot 10^{-4}$

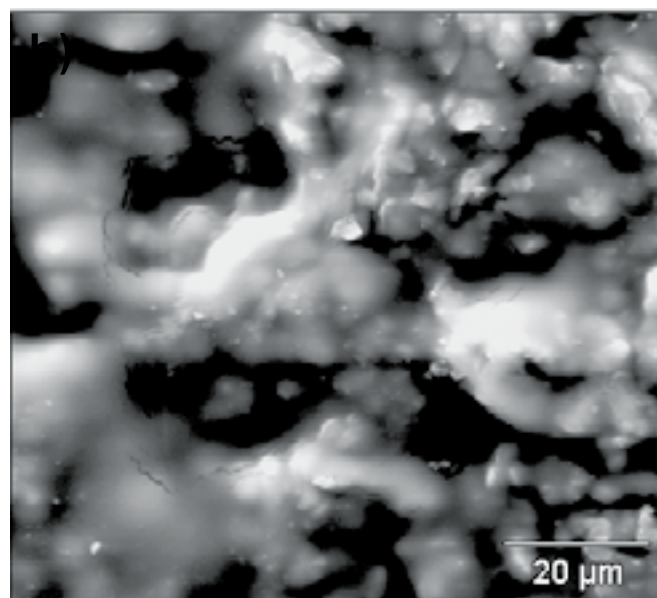
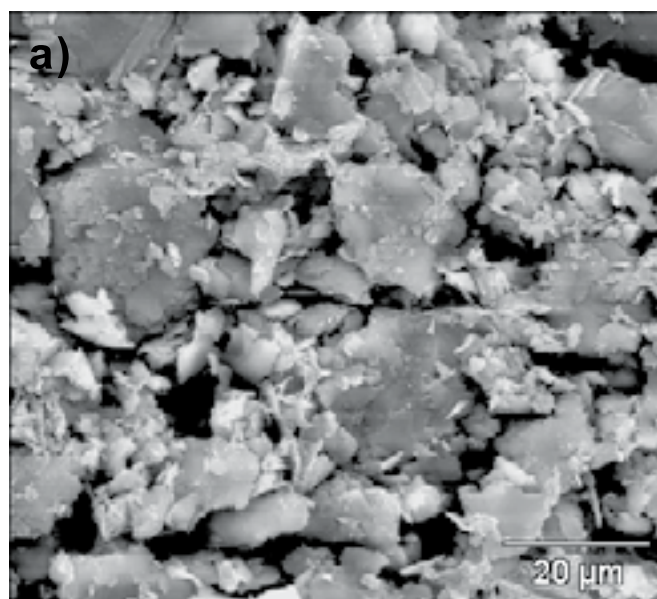


Fig. 4- SEM micrographs of the top surface of a) 90/10 and b) 50/50 self supported carbon electrodes.

### 3.3 Electrochemical behaviour of self-supported carbon electrodes

Self-supported carbon electrode with 90/10 graphite/organics ratio was chosen for the electrochemical characterization of norepinephrine oxidation in basis of its high conductivity.

Figure 5 depicts the cyclic voltammetry curve of norepinephrine obtained with the 90/10 self-supported carbon electrode applying a voltage scan from -0.400 V to 0.600 V and vice versa. The oxidation peak of norepinephrine was clearly observed at  $\sim 0.380$  V whereas the reduction one was observed at  $\sim 0.190$  V. The cyclic voltammogram of the buffer solution is also included for comparison. As it can be seen, there was not interaction between the working electrode (self-supported carbon electrode) and the buffer solution. These curves are a clear indication that self-supported carbon electrode is working properly showing the redox reactions of norepinephrine.

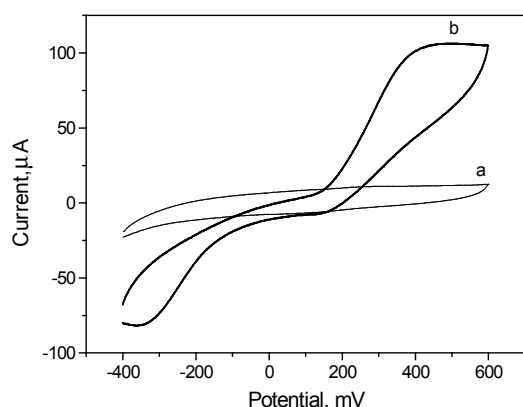


Fig. 5- Cyclic voltammetry curve of norepinephrine obtained with the 90/10 self-supported carbon electrode.

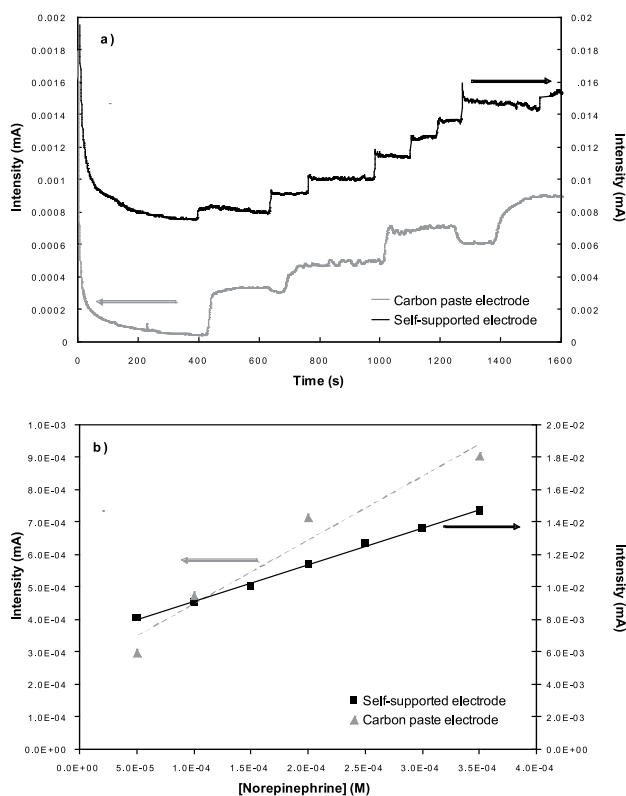


Fig. 6- a) Amperometric curves obtained from both types of electrodes as a function of the molarity of the norepinephrine solution. b) Calibration curves.

During the amperometric studies a working potential of 0.500 V was selected. In this case, working electrode was 90/10 self-supported carbon electrode and for comparison, a traditional 90/10 carbon paste electrode was also used. Figure 6.a shows the amperometric curves obtained from both types of electrodes. As it can be observed, self-supported carbon electrodes presented higher net intensity current (mA) which increased with each norepinephrine addition ( $1 \cdot 10^{-5}$  M). On the contrary, carbon paste electrodes showed very low sensibility. Taking into account these preliminary results, self-supported carbon electrodes could be a good choice as amperometric sensors in flowing solutions. Figure 6.b shows calibration curve obtained for both types of electrodes. As it can be seen, the response of the self-supported carbon electrode was linear and sensible to the seven additions, whereas the traditional carbon paste electrode was less sensible, only some of the additions were registered as well as the response was not linear.

#### 4. CONCLUSIONS

Self-supported carbon electrodes, a new type of electrochemical sensors, have been prepared by tape casting. Electrical conductivity of these electrodes have been characterized and related to the graphite content in the green tapes. The dc electrical conductivity decreased with the increase of organic additives in the tapes due to the formation of an isolating film which impedes the charge transfer among the graphite particles. The electrode with higher conductivity (higher graphite content) was chosen to characterize the electrochemical response of self-supported carbon electrodes. The electroanalytical behaviour was evaluated in cyclic voltammetry and amperometry using a norepinephrine solution. The redox reactions of norepinephrine on the self-supported carbon electrode were clearly observed in the voltammograms. Besides, the sensibility during the amperometric runs was higher than that showed by the traditional carbon paste electrodes (CPEs) with the same graphite content. These results indicate that this new type of electrochemical sensors, the self-supported carbon electrodes fabricated by tape casting method, are a good alternative for working electrodes in different electroanalytical techniques.

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#### REFERENCES

1. R. Adams, "Carbon Paste Electrodes", *Anal. Chem.* 30, 1576 (1958).
2. K. Kalcher, "Chemically Modified Carbon Paste Electrodes in Voltammetric Electroanalysis", *Electroanalysis*, 2(6), 419-433 (1990).
3. K. Kalcher, J.M., Kauffmann, J. Wang, I. Svankara, K. Vytras, C. Neuhold and Z. Yang. "Sensors based on Carbon-Paste in Electrochemical Analysis - A Review with Particular Emphasis on the period 1990-1993". *Electroanalysis*, 7(1), 5-22 (1995).
4. W. Matuszewski, M. Trojanowicz. "Graphite Paste-based Enzymatic Glucose Electrode for Flow-Injection Analysis". *Analyst*, 113(5), 735-738 (1988).

5. Z.Q. Zhang, H. Liu, H. Zhang, Y.F. Li. "Simultaneous Cathodic Stripping Voltammetric Determination of Mercury, Cobalt, Nickel and Palladium by Mixed Binder Carbon Paste Electrode containing Dimethylglyoxime". *Anal. Chim. Acta.*, 333(1-2), 119-124 (1996).
6. J.C. Williams, in *Ceramic Fabrication Processes*, Vol. 9, ed. F.F.Y. Wang. Academic Press, New York, 1976, pp.173-198.
7. R.E. Mistler, E.R. Twinn. "Tape Casting. Theory and Practice". The American Ceramic Society, Inc. Westerville, OH 2000.
8. H. Jantunen, T. Hu, A. Uusimäki, S. Leppävuori. "Tape Casting of Ferroelectric, Dielectric, Piezoelectric and Ferromagnetic Materials", *J. Europ. Ceram. Soc.*, 24, 1077-1081 (2004).
9. J.F. Fernández, P. Durán, C. Moure. "Microstructure Development of Tape Casting BaTiO<sub>3</sub> Ceramics". *Ferroelectrics* 127, 65-70 (1992).
10. E. Solera, T. Jardiel, M. Villegas, J.F. Fernández. "Influencia de las Diferentes Etapas de Procesamiento sobre la Microestructura de Dispositivos Multicapa basados en PZT". *Bol. Soc. Esp. Ceram.* V. 41, 1, 166-170 (2002).
11. R.B. Runk, M.J. Andrejco. "A Precision Tape Casting Machine for Fabricating Thin Ceramic Tapes". *Am. Ceram. Soc. Bull.*, 54(2), 199-200 (1975).
12. J. Jiménez, M. Poyatos, J.F. Fernández. "Sistemas de Precisión para Colado en Cinta de Materiales Cerámicos Avanzados". *Bol. Soc. Esp. Ceram.* V. 33, 1, 44-52 (1994).
13. *Low Level Measurements Handbook*. Precision DC Current, Voltage and Resistance Measurements. 6th Edition. Section 3, p. 3-18. Kethley Instruments Inc. Cleveland, OH. 2004.

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